

# Energy Current Correlations For Weakly Anharmonic Lattices<sup>1</sup>

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## 1 Introduction

A solid transports energy. Besides the mobile electrons, one important mechanism for energy transport are the vibrations of the crystal lattice. There is no difficulty in writing down the appropriate lattice dynamics. To extract from it the thermal conductivity remains a fairly untractable problem. The most successful approach exploits that even rather close to the melting temperature the typical deviations of the crystal atoms from their equilibrium position are small as compared to the lattice constant. This observation then leads to the phonon kinetic equation, which goes back to the seminal paper by Peierls [1]. (For electron transport a corresponding idea was put forward by Nordheim [2].) Phonon kinetic theory flourished in the 50ies, an excellent account of the 1960 status being the book by Ziman [3]. Of course, transport of heat and thermal conductivity remain an important experimental research area, in particular since novel materials become available and since more extreme properties are in demand. On the other hand, if the very recent collection of articles by Tritt [4] is taken to be representative, it is obvious that after 1960 hardly any new elements have been added to the theory. The real innovation are fast and efficient molecular dynamics algorithms. The currently available techniques allow the simulation of  $6 \times 6 \times 6$  periodized lattices with two atoms per unit cell [5].

According to the Green-Kubo formula the thermal conductivity is determined through the time-integral over the energy current correlation in thermal equilibrium. In my contribution I will explain its structure for weakly anharmonic lattices. While I do not add anything novel in substance, I believe that, with the post 1960 insights gained from the kinetic theory of rarified gases, the story can be presented more concisely and systematically than done usually. As a bonus, the mathematical physics issues left unresolved will become more sharply in focus.

## 2 Anharmonic lattice dynamics

Physically, one starts from a given crystal structure, which means to specify the lattice and the number of atoms per unit cell. The interaction potential is expanded

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in the displacements away from the equilibrium positions. Then the first order term vanishes, because one expands at a stationary point. The second order term is the harmonic approximation and higher order terms are regarded as small corrections. It is argued that for real crystals mostly the third order term suffices unless there are special symmetries which make it vanish and requires to go to fourth order. In this article, the focus will be on the analysis of the linearized Boltzmann equation and its relation to the energy current correlations. For this purpose we take the liberty to employ a single band model for the anharmonic lattice dynamics. There is no difficulty, in principle, to add on extra features so to make the model more realistic.

We assume a simple hypercubic lattice  $\mathbb{Z}^d$  with a single atom per unit cell. Physically  $d = 3$ , but we keep the general dimension  $d$  because of recent interest in chains, for which  $d = 1$ . A single band model corresponds to scalar atomic displacements.

Fourier transform will be convenient. Let  $\mathbb{T}^d = [-\frac{1}{2}, \frac{1}{2}]^d$  be the first Brioullin zone of the dual lattice. For  $f : \mathbb{Z}^d \rightarrow \mathbb{R}$  its Fourier transform,  $\hat{f}$ , is defined by

$$\hat{f}(k) = \sum_{x \in \mathbb{Z}^d} e^{-i2\pi k \cdot x} f_x. \quad (2.1)$$

Here  $k \in \mathbb{T}^d$  and  $\hat{f}(k)$  extends periodically to a function on  $\mathbb{R}^d$ . The inverse Fourier transform is given by

$$f_x = \int_{\mathbb{T}^d} dk e^{i2\pi k \cdot x} \hat{f}(k). \quad (2.2)$$

For  $x \in \mathbb{Z}^d$  the deviation away from  $x$  is denoted by  $q_x \in \mathbb{R}$ . The corresponding momentum is denoted by  $p_x \in \mathbb{R}$ . We choose units such that the atomic mass equals one. The harmonic approximation to the interaction potential reads

$$U_{\text{harm}}(q) = \frac{1}{2} \sum_{x, y \in \mathbb{Z}^d} \alpha(x - y) q_x q_y. \quad (2.3)$$

The elastic constants  $\alpha(x)$  satisfy

$$\alpha(x) = \alpha(-x), \quad |\alpha(x)| \leq \gamma_0 e^{-\gamma_1 |x|} \quad (2.4)$$

for suitable constants  $\gamma_0, \gamma_1 > 0$ . Mechanical stability requires

$$\hat{\alpha}(k) \geq 0. \quad (2.5)$$

In addition, because of the invariance of the interaction between crystals atoms under the translation  $q_x \rightsquigarrow q_x + a$ , one imposes

$$\sum_{x \in \mathbb{Z}^d} \alpha(x) = 0, \quad \text{i.e.} \quad \hat{\alpha}(0) = 0. \quad (2.6)$$

For an optical band, because of the internal structure of the unit cell, the condition (2.6) is not satisfied, which in the framework of our model can be interpreted as adding to the physical harmonic interaction satisfying (2.6) a harmonic on-site potential of the form

$$U_{\text{site}}(q) = \frac{1}{2} \omega_0^2 \sum_{x \in \mathbb{Z}^d} q_x^2. \quad (2.7)$$

The harmonic lattice dynamics is governed by the hamiltonian

$$H_{\text{ha}} = \frac{1}{2} \sum_{x \in \mathbb{Z}^d} (p_x^2 + \omega_0^2 q_x^2) + \frac{1}{2} \sum_{x, y \in \mathbb{Z}^d} \alpha(x - y) q_x q_y \quad (2.8)$$

and has plane wave solutions with dispersion relation

$$\omega(k) = (\omega_0^2 + \hat{\alpha}(k))^{1/2}. \quad (2.9)$$

Clearly,  $\omega(k) = \omega(-k)$  and  $\omega(k) \geq \omega_0 \geq 0$ . We concatenate  $q_x$  and  $p_x$  into a single complex-valued field  $a(k)$  as

$$a(k) = \frac{1}{\sqrt{2}} (\sqrt{\omega(k)} \hat{q}(k) + i \frac{1}{\sqrt{\omega(k)}} \hat{p}(k)) \quad (2.10)$$

with the inverse

$$\hat{q}(k) = \frac{1}{\sqrt{2}} \frac{1}{\sqrt{\omega(k)}} (a(k) + a(-k)^*), \quad \hat{p}(k) = \frac{i}{\sqrt{2}} \sqrt{\omega(k)} (-a(k) + a(-k)^*). \quad (2.11)$$

The  $a$ -field evolves as

$$\frac{\partial}{\partial t} a(k, t) = -i \omega(k) a(k, t). \quad (2.12)$$

In nature lattice vibrations are quantized. In our model this is easily implemented by promoting  $a(k)^*$  and  $a(k)$  to creation and annihilation operators of a scalar Bose field.  $a(k)^*$  is the operator adjoint to  $a(k)$  and the  $a(k)$ 's satisfy the canonical commutation relations

$$[a(k), a(k')^*] = \delta(k - k'), \quad [a(k), a(k')] = 0. \quad (2.13)$$

The Heisenberg evolution for the  $a$ -field is still governed by (2.12).

Continuing the expansion scheme we add to  $H_0$  the next order terms. The simplest one would be a cubic on-site potential as

$$V_3 = \frac{1}{3} \sum_{x \in \mathbb{Z}^d} q_x^3, \quad (2.14)$$

which in terms of the  $a$ -field reads

$$V_3 = \frac{1}{3} \int_{\mathbb{T}^{3d}} dk_1 dk_2 dk_3 \delta(k_1 + k_2 + k_3) \prod_{j=1}^3 (2\omega(k_j))^{-1/2} (a(k_j) + a(-k_j)^*). \quad (2.15)$$

Correspondingly, at fourth order,

$$V_4 = \frac{1}{4} \sum_{x \in \mathbb{Z}^d} q_x^4 \quad (2.16)$$

which in terms of the  $a$ -field becomes

$$V_4 = \frac{1}{4} \int_{\mathbb{T}^{4d}} dk_1 dk_2 dk_3 dk_4 \delta(k_1 + k_2 + k_3 + k_4) \prod_{j=1}^4 (2\omega(k_j))^{-1/2} (a(k_j) + a(-k_j)^*) . \quad (2.17)$$

$H_{\text{ha}} + \lambda V_3$  is not bounded from below. This can be remedied by adding  $\lambda^2 V_4$ , for example, which would then not contribute on the kinetic scale.

If the potential depends only on the displacement differences, then the lowest order nonlinearity is

$$V_{3\text{di}} = \frac{1}{3} \sum_{x, y \in \mathbb{Z}^d} \alpha_3(x - y) (q_x - q_y)^3 \quad (2.18)$$

with  $\alpha_3(-x) = -\alpha_3(x)$  and  $|\alpha_3|$  exponentially bounded. Switching to the  $a$ -field  $V_{3\text{di}}$  becomes

$$V_{3\text{di}} = \frac{1}{3} \int_{\mathbb{T}^{4d}} dk_1 dk_2 dk_3 \delta(k_1 + k_2 + k_3) \times \sum_{x \in \mathbb{Z}^d} \alpha_3(x) \prod_{j=1}^3 (2\omega(k_j))^{-1/2} (e^{i2\pi k_j \cdot x} - 1) (a(k_j) + a(-k_j)^*) . \quad (2.19)$$

In the kinetic limit the square of the vertex function determines the collision rate. Thus, from the collision rate

$$\prod_{j=1}^3 (2\omega(k_j))^{-1} \quad (2.20)$$

for the on-site  $V_3$  the collision rate for  $V_{3\text{di}}$  is obtained by the replacement

$$\prod_{j=1}^3 (2\omega(k_j))^{-1} \rightarrow \left| \sum_{x \in \mathbb{Z}^d} \alpha_3(x) \prod_{j=1}^3 (e^{i2\pi k_j \cdot x} - 1) \right|^2 . \quad (2.21)$$

Because of such a simple substitution rule we continue to work with  $V_3$ . The corresponding rule also applies to the switch from  $V_4$  to  $V_{4\text{di}}$ .

From other areas of mathematical physics one is accustomed to have a given starting hamiltonian. In our context this means to specify the elastic constants  $\alpha(x)$ ,  $\alpha_3(x)$ ,  $\alpha_4(x)$ . For real crystals their determination requires a lot of experimental (and also theoretical) efforts, as discussed in [4], see also [6, 7, 8] for a modeling of aluminium and silicon. It would be thus of importance to have a stability result available, which ensures that certain qualitative properties do not depend so much on the specific choice of elastic constants.

### 3 Energy current correlations

Let us consider the Hamiltonian

$$H = H_{\text{ha}} + \lambda V_3 + \lambda^2 V_4. \quad (3.1)$$

The total energy current correlation function is computed in thermal equilibrium at inverse temperature  $\beta$ . It is denoted by  $C_\lambda(t)$  and will be defined below. Since  $\lambda \ll 1$ , the plan is to compute  $C_\lambda(t)$  in the limit of  $\lambda \rightarrow 0$ . The phonons then hardly interact and  $C_\lambda(t)$  decays slowly on the time scale  $\lambda^{-2}$ . Thus one expects that the limit

$$\lim_{\lambda \rightarrow 0} C_\lambda(\lambda^{-2}t) = C_{\text{kin}}(t) \quad (3.2)$$

exists and is determined by the phonon Boltzmann equation linearized at equilibrium.

Let us first find the local energy current. Since  $H$  is not local, there is some arbitrariness involved in defining the local energy. One conventional choice for the energy at site  $x$  is to set

$$H_x = \frac{1}{2}p_x^2 + \frac{1}{2}\omega_0^2 q_x^2 + \frac{1}{2} \sum_{y \in \mathbb{Z}^d} \alpha(x-y) q_x q_y + \frac{1}{3} \lambda q_x^3 + \frac{1}{4} \lambda^2 q_x^4. \quad (3.3)$$

In the Heisenberg picture  $H_x$  becomes time-dependent. Writing  $dH_x(t)/dt$  as a divergence, the energy current can be identified with

$$J_x = \frac{1}{4} \sum_{y \in \mathbb{Z}^d} y \alpha(y) (-q_x p_{x+y} + q_{x+y} p_x) \quad (3.4)$$

which happens to be independent of  $\lambda$ . To verify (3.4), one chooses a large box  $\Lambda$  with faces  $\partial\Lambda$ . The energy inside  $\Lambda$  is

$$H_\Lambda(t) = \sum_{x \in \Lambda} H_x(t) \quad (3.5)$$

and it satisfies

$$\frac{d}{dt} H_\Lambda(t) = - \sum_{x \in \Lambda} n_x \cdot J_x(t) + \mathcal{O}(\partial\Lambda), \quad (3.6)$$

where  $n_x$  is the outward normal to  $\Lambda$  at  $x \in \partial\Lambda$ . The errors come from the corners of  $\Lambda$  and from the possibly infinite range of  $\alpha$ .

With this input the total energy current correlation is defined by

$$\ell \cdot C_\lambda(t) \ell = \sum_{x \in \mathbb{Z}^d} \langle (\ell \cdot J_0(t)) (\ell \cdot J_x(0)) \rangle_\beta, \quad (3.7)$$

where  $\ell \in \mathbb{R}^d$ ,  $J_x \in \mathbb{R}^d$ , “ $\cdot$ ” is the scalar product in  $\mathbb{R}^d$ , and  $C_\lambda(t)$  is a  $d \times d$  matrix.  $\langle \cdot \rangle_\beta$  refers to the thermal average with respect to  $Z^{-1} e^{-\beta H}$ . By time-stationary and

time-reversal,  $C_\lambda(t)$  is symmetric and it suffices to consider its numerical range. At the expense of an error of order  $\lambda$ , we may replace in  $e^{-\beta H}$  the full Hamiltonian  $H$  by the harmonic approximation

$$H_{\text{ha}} = \int_{\mathbb{T}^d} dk \omega(k) a(k)^* a(k). \quad (3.8)$$

For the total current one finds

$$J = \sum_{x \in \mathbb{Z}^d} J_x = \frac{1}{2\pi} \int_{\mathbb{T}^d} dk (\nabla \omega(k)) \omega(k) a(k)^* a(k), \quad (3.9)$$

where it is used that  $\nabla \hat{\alpha} = 2\omega(\nabla \omega)$ . Since  $[H_{\text{ha}}, J] = 0$ ,  $\sum_{x \in \mathbb{Z}^d} \ell \cdot J_x$  can be lifted to the exponent. Thus we define the new average  $\langle \cdot \rangle_{\beta, \tau}$  with respect to the state  $Z^{-1} \exp[-\beta H_{\text{ha}} + \tau \ell \cdot J]$ . Then

$$\ell \cdot C_\lambda(t) \ell = \lim_{\tau \rightarrow 0} \frac{1}{\tau} \langle \ell \cdot J_0(t) \rangle_{\beta, \tau} + \mathcal{O}(\lambda). \quad (3.10)$$

The anharmonicity now resides only in the dynamics.

The limit  $\lambda \rightarrow 0$  on the right hand side in (3.10) is discussed in [9]. The initial state is spatially homogeneous and determines the Wigner function  $W_{\beta, \tau}(k)$  through

$$\langle a(k')^* a(k) \rangle_{\beta, \tau} = \delta(k - k') W_{\beta, \tau}(k) \quad (3.11)$$

with

$$W_{\beta, \tau}(k) = \left( \exp [\beta \omega(k) - \tau (\ell \cdot \nabla \omega(k)) \omega(k)] - 1 \right)^{-1}. \quad (3.12)$$

On the kinetic time scale,  $\lambda^{-2}t$ , the Wigner function  $W_{\beta, \tau}$  evolves to  $W_\tau(t)$  which is determined as the solution of the spatially homogeneous Boltzmann equation. For our model, i.e. for the anharmonic on-site potential  $V_3$ , it reads

$$\frac{\partial}{\partial t} W(t) = \mathcal{C}(W(t)) \quad (3.13)$$

with the collision operator

$$\begin{aligned} \mathcal{C}(W)_1 &= \frac{\pi}{2} \int_{\mathbb{T}^{2d}} dk_2 dk_3 (\omega_1 \omega_2 \omega_3)^{-1} \\ &\quad \times \left\{ 2\delta(\omega_1 + \omega_2 - \omega_3) \delta(k_1 + k_2 - k_3) (\tilde{W}_1 \tilde{W}_2 W_3 - W_1 W_2 \tilde{W}_3) \right. \\ &\quad \left. + \delta(\omega_1 - \omega_2 - \omega_3) \delta(k_1 - k_2 - k_3) (\tilde{W}_1 W_2 W_3 - W_1 \tilde{W}_2 \tilde{W}_3) \right\}. \end{aligned} \quad (3.14)$$

Here we use the shorthands  $W_j = W(k_j)$ ,  $\omega_j = \omega(k_j)$ ,  $j = 1, 2, 3$ , and  $\tilde{W}(k) = 1 + W(k)$ . Using (3.9), the average in (3.10) becomes then

$$\langle \ell \cdot J_0(\lambda^{-2}t) \rangle_{\beta, \tau} = \frac{1}{2\pi} \int_{\mathbb{T}^d} dk (\ell \cdot \nabla \omega(k)) \omega(k) W_\tau(k, t) + \mathcal{O}(\lambda). \quad (3.15)$$

The next task is to take the limit  $\tau \rightarrow 0$  in (3.10). One has  $W_{\beta,0}(k) = (e^{\beta\omega(k)} - 1)^{-1}$  which is a stationary solution of (3.13). Thus the limit  $\tau \rightarrow 0$  amounts to linearize (3.14) at the equilibrium Wigner function

$$W_{\beta}(k) = (e^{\beta\omega(k)} - 1)^{-1}, \quad (3.16)$$

to say

$$W_{\beta,\tau} = W_{\beta} + \tau W_{\beta} \tilde{W}_{\beta} (\ell \cdot \nabla \omega) \omega + \mathcal{O}(\tau^2). \quad (3.17)$$

Note that  $\int dk (\nabla \omega) \omega W_{\beta} = 0$ . As suggested by (3.17), with a significance which will become more convincing in the context of the Gaussian fluctuation theory, see Section 5, the natural linearization of  $\mathcal{C}$  is

$$\mathcal{C}(W_{\beta} + \delta W_{\beta} \tilde{W}_{\beta} f) = -\delta L f + \mathcal{O}(\delta^2). \quad (3.18)$$

From (3.14) one deduces

$$\begin{aligned} (Lf)_1 &= \frac{\pi}{2} \int_{\mathbb{T}^{2d}} dk_2 dk_3 (\omega_1 \omega_2 \omega_3)^{-1} \\ &\quad \times (2\delta(\omega_1 + \omega_2 - \omega_3) \delta(k_1 + k_2 - k_3) \tilde{W}_{\beta 1} \tilde{W}_{\beta 2} W_{\beta 3} (f_1 + f_2 - f_3) \\ &\quad + \delta(\omega_1 - \omega_2 - \omega_3) \delta(k_1 - k_2 - k_3) \tilde{W}_{\beta 1} W_{\beta 2} W_{\beta 3} (f_1 - f_2 - f_3)). \end{aligned} \quad (3.19)$$

Properties of  $L$  will be discussed in the subsequent section.

Let  $A$  be the linear operator obtained from flat linearization as

$$\mathcal{C}(W_{\beta} + \delta f) = \delta A f + \mathcal{O}(\delta^2). \quad (3.20)$$

Clearly  $A(W_{\beta} \tilde{W}_{\beta} f) = -L f$ . Combining (3.10) and (3.15) we finally conclude

$$\lim_{\lambda \rightarrow 0} \ell \cdot C_{\lambda}(\lambda^{-2} t) \ell = \ell \cdot C_{\text{kin}}(t) \ell \quad (3.21)$$

with

$$\ell \cdot C_{\text{kin}}(t) \ell = \langle (2\pi)^{-1} (\ell \cdot \nabla \omega) \omega, e^{-A|t|} W_{\beta} \tilde{W}_{\beta} (2\pi)^{-1} (\ell \cdot \nabla \omega) \omega \rangle, \quad (3.22)$$

where  $\langle \cdot, \cdot \rangle$  is the inner product in  $L^2(\mathbb{T}^d, dk)$ .

For future use it will be convenient to write  $C_{\text{kin}}(t)$  in a more symmetric form. Expanding the exponential one notes that

$$\begin{aligned} \ell \cdot C_{\text{kin}}(t) \ell &= \langle (2\pi)^{-1} (\ell \cdot \nabla \omega) \omega (W_{\beta} \tilde{W}_{\beta})^{1/2}, \\ &\quad \exp \left[ - (W_{\beta} \tilde{W}_{\beta})^{-(1/2)} L (W_{\beta} \tilde{W}_{\beta})^{-(1/2)} |t| \right] (W_{\beta} \tilde{W}_{\beta})^{1/2} (2\pi)^{-1} (\ell \cdot \nabla \omega) \omega \rangle. \end{aligned} \quad (3.23)$$

As will be shown,  $L = L^*$ , i.e.  $L$  is a symmetric operator in  $L^2(\mathbb{T}^d, dk)$ . Therefore  $C_{\text{kin}}(t)$  is a positive symmetric  $d \times d$  matrix.

In the kinetic limit the thermal conductivity is given through

$$\begin{aligned}\ell\kappa_{\text{kin}} \cdot \ell &= \beta^2 \int_0^\infty dt \ell \cdot C_{\text{kin}}(t) \ell \\ &= (2\pi)^{-2} \beta^2 \langle (\ell \cdot \nabla \omega) \omega W_\beta \tilde{W}_\beta, L^{-1}(\ell \cdot \nabla \omega) \omega W_\beta \tilde{W}_\beta \rangle.\end{aligned}\quad (3.24)$$

Reversing our argument, and assuming uniformity in  $t$  for the limit  $\lambda \rightarrow 0$ , one infers that the true thermal conductivity,  $\kappa(\lambda)$ , of the anharmonic model behaves as

$$\kappa(\lambda) \cong \lambda^{-2} \kappa_{\text{kin}} \quad (3.25)$$

for small  $\lambda$ .

In the classical limit  $[a(k), a(k')^*] = 0$ , i.e.,  $W = \tilde{W}$ . In the definition of  $L$  one has thus to replace

$$W_\beta, \tilde{W}_\beta \quad \text{by} \quad W_\beta^{\text{cl}}(k) = \frac{1}{\beta\omega(k)}. \quad (3.26)$$

We presented the argument for a cubic on-site potential. But, clearly, the result holds also for other small anharmonicities. Only the collision operator, and its linearization  $L$ , would have to be modified.

## 4 The linearized collision operator

If one accepts the argument leading to (3.21), the remaining task is to study the spectral properties of the linearized collision operator, from which the time decay of  $C_{\text{kin}}(t)$  can be inferred. While this looks like a conventional mathematical physics problem, the difficulty comes from the energy-momentum constraint. Only in a few special cases there is an explicit solution. Otherwise one has to work with the implicit definition. In fact, there can be no solution at all, in which case  $L = 0$ , or several solutions, in which case one has to sum over all collision branches.

(i) *quadratic form.* For three phonon processes, on-site potential  $V_3$ , the quadratic form of the linearized collision operator  $L = L_3$  is given by

$$\begin{aligned}\langle g, L_3 f \rangle &= \frac{\pi}{2} \int_{\mathbb{T}^{3d}} dk_1 dk_2 dk_3 (\omega_1 \omega_2 \omega_3)^{-1} \delta(\omega_1 + \omega_2 - \omega_3) \delta(k_1 + k_2 - k_3) \\ &\quad \times W_{\beta 1} W_{\beta 2} \tilde{W}_{\beta 3} (g_1 + g_2 - g_3) (f_1 + f_2 - f_3).\end{aligned}\quad (4.1)$$

Correspondingly for the on-site potential  $V_4$  one has

$$\begin{aligned}\langle g, L_4 f \rangle &= \frac{3\pi}{4} \cdot \frac{3}{4} \int dk_1 dk_2 dk_3 dk_4 (\omega_1 \omega_2 \omega_3 \omega_4)^{-1} \delta(\omega_1 + \omega_2 - \omega_3 - \omega_4) \delta(k_1 + k_2 - k_3 - k_4) \\ &\quad \times W_{\beta 1} W_{\beta 2} \tilde{W}_{\beta 3} \tilde{W}_{\beta 4} (g_1 + g_2 - g_3 - g_4) (f_1 + f_2 - f_3 - f_4) \\ &\quad + \frac{3\pi}{4} \int dk_1 dk_2 dk_3 dk_4 (\omega_1 \omega_2 \omega_3 \omega_4)^{-1} \delta(\omega_1 + \omega_2 + \omega_3 - \omega_4) \delta(k_1 + k_2 + k_3 - k_4) \\ &\quad \times W_{\beta 1} W_{\beta 2} W_{\beta 3} \tilde{W}_{\beta 4} (g_1 + g_2 + g_3 - g_4) (f_1 + f_2 + f_3 - f_4) \\ &= \langle f, L_{4p} f \rangle + \langle f, L_{4t} f \rangle.\end{aligned}\quad (4.2)$$



$L_{4p}$  corresponds to the collision of a pair of phonons and  $L_{4t}$  to a merger of three phonons into a single one, and its time reversal. The quadratic forms for  $L_3, L_{4p}, L_{4t}$  (for notational simplicity from now on commonly denoted by  $L$ ) are somewhat formal. Firstly, if  $\omega(0) = 0$  and  $\omega(k) > 0$  otherwise, the smooth functions  $g, f$  have to vanish at  $k = 0$ . More seriously, the proper definition of the  $\delta$ -function requires to study more carefully the solutions to the energy constraint

$$\omega(k_1) + \omega(k_2) = \omega(k_1 + k_2), \quad (4.3)$$

say in the case of  $L_3$ . For the purpose of our exposition, let us simply assume that the quadratic form defines  $L$  as a self-adjoint operator. Clearly,  $L \geq 0$  since  $\langle f, Lf \rangle \geq 0$ . As  $(\ell \cdot \nabla \omega)\omega$  is bounded, one has

$$\ell \cdot C_{\text{kin}}(t)\ell \leq (2\pi)^{-2} \langle (\ell \cdot \nabla \omega)\omega, (\ell \cdot \nabla \omega)\omega \rangle. \quad (4.4)$$

(ii) *zero subspace*. To establish that  $\lim_{t \rightarrow \infty} C_{\text{kin}}(t) = 0$ ,  $(\ell \cdot \nabla \omega)\omega$  has to be orthogonal to the zero subspace of  $L$ . There seems to be no cheap argument and one has to study the solutions to

$$Lf = 0. \quad (4.5)$$

From (4.1), (4.2) it follows that  $f$  has to be a collisional invariant, see [9, 10] for the definition. Considering only the first summand of (4.2), there is a general argument [10], that the solutions to  $\langle f, L_{4p}f \rangle = 0$  are spanned by  $1, \omega$ . Note that  $\langle 1, (\ell \cdot \nabla \omega)\omega \rangle = 0$ ,  $\langle \omega, (\ell \cdot \nabla \omega)\omega \rangle = 0$ . The constant function results from phonon number conservation in a pair collision. This conservation law will be destroyed by adding a little bit of either three-phonon,  $L_3$ , or the second term of the four-phonon processes,  $L_{4t}$ . The zero subspace is then one-dimensional and spanned by  $\omega$  only. For  $L_3$  of (4.1), the classification of the collisional invariants is an open problem.

(iii) *spectral gap*. If  $L$  has a spectral gap, the energy current correlation decays exponentially. If in addition  $(\ell \cdot \nabla \omega)\omega$  is orthogonal to the zero subspace of  $L$ , then the conductivity, as the time-integral over  $C_{\text{kin}}(t)$ , is finite (and non-zero). In particular (3.25) holds.

$L$  is a sum of a multiplication operator and an integral operator,

$$L = V + I, \quad Vf(k) = V(k)f(k), \quad If(k) = \int_{\mathbb{T}^d} dk' I(k, k')f(k'), \quad (4.6)$$

where, say in the case of  $L_3$ ,

$$\begin{aligned} V(k) &= \frac{\pi}{2} W_\beta(k) \omega(k)^{-1} \int_{\mathbb{T}^d} dk_1 (\omega(k_1) \omega(k + k_1))^{-1} \\ &\quad \times \left( 2\delta(\omega(k) + \omega(k_1) - \omega(k + k_1)) W_\beta(k_1) \tilde{W}_\beta(k + k_1) \right. \\ &\quad \left. + \delta(\omega(k) - \omega(k_1) - \omega(k + k_1)) \tilde{W}_\beta(k_1) \tilde{W}_\beta(k + k_1) \right). \end{aligned} \quad (4.7)$$

The integral kernel  $I(k, k')$  is implicitly defined. It has no definite sign and tends to be divergent on lower-dimensional submanifolds of  $\mathbb{T}^d \times \mathbb{T}^d$ . It would be useful to know under what conditions the integral operator  $I$  is compact.

In the very common relaxation time approximation,  $I$  is simply dropped and one sets in approximation

$$\ell \cdot C_{\text{kin}}(t)\ell = (2\pi)^{-2} \langle (\ell \cdot \nabla \omega) \omega, e^{-|t|/\tau} (\ell \cdot \nabla \omega) \omega \rangle \quad (4.8)$$

with the relaxation time

$$\tau(k) = W_\beta(k) \tilde{W}_\beta(k) V(k)^{-1}, \quad (4.9)$$

see (3.23).

(iv) *FPU chains*. The Fermi-Pasta-Ulam chain is the special case  $d = 1$  with nearest neighbor coupling and no quantization. For a harmonic on-site potential the dispersion relation is  $\omega(k) = (\omega_0^2 + 1 - \cos(2\pi k))^{1/2}$ ,  $k \in \mathbb{T}$ . Although  $d = 1$ , the conservation laws of energy and momentum allow for non-degenerate pair collision and  $L_{4p} \neq 0$ , while  $L_{4t} = 0$  [11, 12, 13]. There are fairly explicit formulae for the potential  $V$  and the integral kernel  $I$  [14]. For  $\omega_0 > 0$  and a quartic on-site potential  $V_4$ , the linearized collision operator has a gap and the zero subspace is two-dimensional. The gap seems to close as  $\omega_0 \rightarrow 0$ . On the basis of numerical simulations, the conductivity should be finite even for  $\omega_0 = 0$  [12]. The FPU- $\beta$  chain has the nonlinearity  $V_{\text{di4}}$ .  $V$  and  $I$  has been computed by Pereverzev [11]. He uses the relaxation time approximation and finds that  $C_{\text{kin}}(t) \cong t^{-3/5}$  for large  $t$ . Using a resolvent expansion, in [13] we prove corresponding sharp bounds and thereby confirm the relaxation time approximation in this particular case. For a finite chain of length  $N$  with thermal reservoirs at both ends, the energy transport is then anomalous and the thermal conductivity diverges as  $N^{2/5}$ , which seems to be in agreement with molecular dynamics. For a more detailed discussion we refer to [15], Section 6.

## 5 Gaussian fluctuation theory

Energy transport can be viewed in the more general context of time-dependent Gaussian fluctuation theory close to thermal equilibrium. For low density gases this link is reviewed in [16] with further examples discussed in [17]. The purpose of this section is to explain how phonon kinetic theory makes no exception. In [16, 17] spatial variation is included. Since our exposition deals only with the spatially homogeneous system, we stick to such a set-up also for the fluctuation theory.

Physically, one considers time-dependent fluctuations in equilibrium for the number of phonons with wave number  $k$ . Technically one has to sum over phonons in a small volume element in  $k$ -space. To be more precise we partition the torus  $\mathbb{T} = [-1/2, 1/2]$  by a grid with spacing  $\varepsilon$  and denote it by  $\mathbb{T}_\varepsilon$ .  $(\mathbb{T}_\varepsilon)^d$  corresponds to

the crystal volume  $[1, \dots, l]^d \subset \mathbb{Z}^d$  with periodic boundary conditions,  $l = 1/\varepsilon$ . Let  $f : \mathbb{T}^d \rightarrow \mathbb{R}$  be a smooth test function. Then the fluctuation field, indexed by  $f$  and  $t$ , is defined through

$$\xi^\varepsilon(f, t) = \varepsilon^{d/2} \sum_{k \in (\mathbb{T}_\varepsilon)^d} f(k) (a^\varepsilon(k, t)^* a^\varepsilon(k, t) - \langle a^\varepsilon(k)^* a^\varepsilon(k) \rangle_\beta). \quad (5.1)$$

$a^\varepsilon(k, t)$  depends on  $\varepsilon$  through the finite crystal volume  $\varepsilon^{-d}$ , through setting  $\lambda^2 = \varepsilon$ , and through the rescaled time  $\varepsilon^{-1}t$  in microscopic units. The claim is that, in distribution, the limit

$$\lim_{\varepsilon \rightarrow 0} \xi^\varepsilon(f, t) = \xi_t(f) \quad (5.2)$$

exists and that the limit random field  $\xi_t(f)$  is classical. In fact, the limit field should be jointly Gaussian and governed by the linear Langevin equation

$$\frac{\partial}{\partial t} \xi_t(k) = A \xi_t(k) + B \eta_t(k), \quad (5.3)$$

where  $\xi_t(f) = \int_{\mathbb{T}^d} dk f(k) \xi_t(k)$ .  $A$  is the generator from the linearized Boltzmann equation, compare with (3.20), and  $\eta_t$  is normalized Gaussian white noise with

$$\mathbb{E}(\eta_t(k) \eta_{t'}(k')) = \delta(t - t') \delta(k - k'). \quad (5.4)$$

The linear operator  $B$  controls the strength and correlations for the noise input to the various  $k$ -modes.

The main observation of the fluctuation theory is the relationship between  $A$  and  $B$  through the equal-time equilibrium fluctuations. We set, as a linear operator,

$$\langle g, Cf \rangle = \lim_{\varepsilon \rightarrow 0} \langle \xi^\varepsilon(g, 0) \xi^\varepsilon(f, 0) \rangle_\beta. \quad (5.5)$$

Using that

$$\begin{aligned} & \langle a^*(k_1) a(k_2) a^*(k_3) a(k_4) \rangle_\beta - \langle a^*(k_1) a(k_2) \rangle_\beta \langle a(k_3)^* a(k_4) \rangle_\beta \\ &= \delta(k_1 - k_4) \delta(k_2 - k_3) W_\beta(k_1) \tilde{W}_\beta(k_2), \end{aligned} \quad (5.6)$$

one obtains

$$\langle g, Cf \rangle = \int_{\mathbb{T}^d} dk g(k) W_\beta(k) \tilde{W}_\beta(k) f(k), \quad (5.7)$$

in other words  $C$  is the operator of multiplication by  $W_\beta \tilde{W}_\beta$ . The fluctuation-dissipation relation takes then the form

$$AC + CA^* = -BB^*. \quad (5.8)$$

Since  $AC = L = L^* = CA^*$ , one concludes that the noise strength is

$$BB^* = 2L. \quad (5.9)$$

A posteriori this identity explains also the at first sight unexpected linearization in (3.18). Only then the linearized operator is symmetric, as is obvious from (5.9).

Solving (5.3), the covariance of the stationary fluctuation field is given by

$$\langle \xi_t(g) \xi_0(f) \rangle = \langle g, e^{A|t|} C f \rangle, \quad (5.10)$$

in agreement with the special case  $f = g = (2\pi)^{-1}(\ell \cdot \nabla \omega) \omega$  of interest in Section 3.

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